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Inventor(s):	Tadeusz Wilczewski
Grantee:	Politechnika Gdanska, Gdansk, Poland

Title of the Invention:

METHOD FOR PRODUCING RUTHENOCENE

The object of the invention is a method of producing ruthenocene.

A method of obtaining ruthenocene is known in the literature (D. E. Bublitz, W. E. McEwen, and J. Kleinberg, *Organic Synth.*, Vol. 41, p. 96, 1961). It is based on the reaction of ruthenium trichloride with cyclopentadiene and metallic sodium. The synthesis takes place in a neutral gas atmosphere in a 1,2-dimethoxyethane medium. After 80 hours of heating, yellow ruthenocene crystals are obtained in a yield of 56-69%.

The ruthenium trichloride used in the reaction is obtained in the partial chlorination of metallic ruthenium.

Purification of the ruthenocene obtained requires the use of sublimation (13 Pascals) and chromatography.

According to the invention, the method of producing ruthenocene is based on the conversion of (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) hydride or halide, advantageously chloride, of general formula 1 presented in the Figure, in which X designates hydrogen or a halogen and L designates triphenylphosphine, into ruthenocene by heating (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) hydride or halide in a medium of aromatic and/or aliphatic hydrocarbons at the boiling point of the solvent.

An alternative production method is based on the conversion of (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) hydride or halide of the general formula presented in the figure, in which X and L have the above significance, in a medium of aromatic and/or aliphatic hydrocarbons, maintaining a temperature of 25°C for five days. The addition of cyclopentadiene, an alkali metal, especially sodium or potassium, or an alkali metal hydride, especially sodium hydride, to the reaction mixture is advantageous. This increases the ruthenocene yield.

The reaction is conducted in a medium of aromatic and/or aliphatic hydrocarbons such as benzene, toluene, or *n*-hexane. The alkali metal and cyclopentadiene are advantageously used in a molar excess of several times relative to ruthenium. Ruthenocene is separated from the reaction mixture by means of a chromatographic column filled with silica gel. The first fraction, which is colorless, after evaporation is ruthenocene in a yield up to 55 wt.%.

The dependence of the yield of ruthenocene synthesis on the presence of a molar excess of cyclopentadiene in the reaction medium is illustrated by the graph as well as the following table.

If there is a cyclopentadiene deficiency (n = 0), ruthenocene is formed in a low yield of 1-5% (graph).

The table characterizes the influence of the holding time of the specimens at 25°C on the ruthenocene yield, in the case of a lack of cyclopentadiene in the reaction medium.

Holding Time, in days	% of Ruthenocene Yield
Dni	%
5	1.8
7	4.7
13	2.8
20	4.7
178	3.9
270	4.0

It unexpectedly turned out that the addition of cyclopentadiene above n = i raises the synthesis yield to about 50%, independently of an increasing molar excess of the cyclopentadiene added.

This is demonstrated in the graph, in which the Y axis designates the ruthenocene yield in wt.% and the X axis designates the molar excess of cyclopentadiene. Curve *1* plots the dependence of the reaction yield on the molar excess of cyclopentadiene for (π-cyclopentadienyl)bis(triphenylphosphine)-ruthenium(II) chloride and curve *2*, for the hydride of this compound.

A similar yield is obtained during several hours of heating at the boiling point of the solvent of the original ruthenium compound with the alkali metal and cyclopentadiene.

The method according to the invention does not require the use of a protective atmosphere, is less time-consuming, and the ruthenocene obtained is of high purity (yellowish-white color) and basically requires no further purification.

The ruthenocene production method according to the invention is illustrated below by implementation examples.

Example 1

(a) The (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) hydride or halide used for ruthenocene synthesis is advantageously obtained as follows.

A mixture of 5 g of powdered metallic ruthenium with 3 g of NaOH is melted in an iron crucible, then 20 g of sodium peroxide is gradually added and the crucible contents are mixed by agitation. The mixture is heated for a half hour at dark red heat. After the melt has cooled, the crucible contents are carefully leached with 5 portions of distilled water (100 mL each). The dark red alkaline solution of sodium ruthenate and perruthenate obtained is set aside for a half hour, after which the liquid over the sediment is decanted.

A distillation unit comprised of a 3-neck flask with a capacity of 2,000 mL, a short water cooler, and two washers with capacities of 1,000 mL and 200 mL is assembled. The first washer is filled with 500 mL of 6 M hydrochloric acid and the second washer is filled with 100 mL of 6 M HCl. The outlet from the last washer is connected to a water pump. The 3-neck flask is equipped with a glass capillary connected with the atmosphere and a separator. The flask contents are heated with an electric heating jacket.

40 g of solid sodium meta-periodate, 100 mL of water, and 30 mL of concentrated sulfuric acid are placed in the distillation flask. By adding the ruthenate solution dropwise through the separator using a slow air flow, the RuO_4 is gradually distilled off, the flask heating is switched on, and the distillation is continued until the entire solution of sodium ruthenate and perruthenate is used up. The reaction of the solution in the flask should remain acidic.

The dark-brown solutions from the first and second washers are combined and the hydrochloric acid is distilled off until one-fourth of the original volume of the solution is reached, then the concentrated solution is poured into a 1,000 mL beaker and evaporated further on an asbestos gauze until a thick syrupy liquid is obtained.

The beaker contents are dissolved in 200 mL of 95% ethanol. After dissolution, the dark-brown solution is filtered. The ruthenium content in the solution obtained should be determined by the conventional method of reduction to the metal and weight determination of the ruthenium in metallic form.

For example, a 0.2 M solution of $RuCl_3$ in 95% ethanol is obtained. Then 16.8 g (64 mM) of triphenylphosphine is placed in a 2,000-mL flask equipped with a reflux condenser and 800 mL of 95% ethanol is added. This is heated to boiling and a solution of 80 mL of 0.2 M $RuCl_3$ in 95% ethanol and 70 mL of 95% (16 mM) is gradually added through the reflux condenser. After 5 minutes of boiling, 150 mL of 95% ethanol containing 20 mL (240 mM) of freshly distilled (42-44°C) cyclopentadiene is added.

The flask contents are further heated for 1 hour. After cooling the flask contents in water with ice, the precipitated, crystalline orange-colored sediment is drained and washed twice with 50 mL of 95% ethanol, water, then again with ethanol and petroleum benzine. The preparation is dried in a desiccator over solid KOH. About 10.5 g of preparation is obtained (90% yield). The preparation obtained in this manner is (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) chloride, with an orange color.

(b) 0.726 g of (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) chloride (1 mM) is poured into a 100-mL flask, 50 mL of benzene is added, and 0.105 g of freshly distilled (42-44°C) cyclopentadiene (7 drops) is weighed out and sodium hydride (0.1648 g of NaH containing 55% paraffin oil is washed with benzene to remove the paraffin oil) is added and it is heated under the reflux condenser at the boiling point of the solvent for 4 hours.

After cooling, the suspension is filtered and the filtrate is passed through a chromatographic column, washing the bed with benzene (S = 0.85 mL, 10 g of silica gel Ø 0.15-0.30 mm). The colorless eluate (80 mL) is collected for 22 minutes. After evaporation of the fraction, 0.128 g of ruthenocene is obtained (colorless flakes) (95% yield).

Example 2

(a) The same as in Example 1.

(b) 0.726 g of (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) chloride is poured into a 100-mL measuring flask, and 50 mL of benzene, 0.089 g of cyclopentadiene, and 0.2 g of sodium hydride are added.

After stirring and closing the flask, it is allowed to stand for 5 days at 25°C. Subsequent procedure as in Example 1, in which case the filter with the sediment is washed with benzene until the volume of colorless eluate reaches 100 mL. After evaporating off the benzene (preferably under reduced pressure), 0.115 g of ruthenocene is obtained (50% yield).

Example 3

(a) The same as in Example 1.

(b) 0.771 g of (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) chloride, 100 mL of toluene, 0.191 g of cyclopentadiene, and 0.22 g of metallic sodium are added to a 150-mL flask. It is heated to boiling under a reflux condenser for 1 hour, the solution is filtered hot, and the toluene is evaporated off under reduced pressure until a dry residue is obtained.

50 mL of benzene is added to the residue and the solution is passed through a chromatographic column (10 g of silica gel), washing the bed with benzene to obtain an eluate volume of 100 mL. After evaporating the benzene

off, 0.098 g of ruthenocene is obtained (42% yield).

Example 4

(a) The same as in Example 1.

(b) 0.720 g of (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) chloride is poured into a 150-mL flask, and 50 mL of *n*-hexane, 0.066 g of cyclopentadiene, and 0.15 g of metallic potassium are added. This mixture is heated at the boiling point of the hydrocarbon under reflux condensing for 6 hours, after which the flask contents are filtered hot. The solvent is removed from the filtrate under reduced pressure to obtain a dry residue, which in turn is dissolved in 50 mL of benzene. The yellow benzene solution is passed through a chromatographic column (procedure as in Example 1) and the bed is washed with benzene until an eluate volume of 80 mL is obtained. The colorless benzene solution is evaporated under reduced pressure to dryness, obtaining 0.0422 g of ruthenocene in the form of colorless flakes (18% yield).

Example 5

(a) The same as in Example 1.

(b) 0.726 g of (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) chloride is weighed into a 150-mL flask and 50 mL of benzene and 0.1253 g of cyclopentadiene are added. It is heated at the boiling point of the solvent under reflux condensing for 4 hours. After cooling, the dark orange-colored solution is filtered through a layer of silica gel (procedure as in Example 1) for 40 minutes; the volume of the first colorless fraction is 70 mL. The spectrophotometrically determined ruthenocene content is 0.078 g (34% yield). After evaporating this fraction, 0.0837 g of a yellowish-white ruthenocene preparation is obtained, which is washed with 1 mL of *n*-hexane. Mp 198-201°C.

Example 6

(a) The same as in Example 1.

(b) 0.726 g of (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) chloride is weighed into a 150-mL flask, 50 mL of benzene is added, and this mixture is heated under reflux cooling at the boiling point of the solvent for 4 hours. After refluxing, the flask contents are filtered through a layer of silica gel (procedure as in Example 1) for 28 minutes; the volume of the first colorless fraction is 63 mL. The spectrophotometrically determined ruthenocene content is 0.001 g (0.4% yield).

Example 7

(a) The (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) hydride or halide used for ruthenocene synthesis is obtained as follows.

2 g of orange-colored (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) chloride is poured into a 500-mL round-bottom flask placed in an assembly with a magnetic stirrer, a magnetic core is introduced, and 100 mL of 0.2 M sodium methanol solution in anhydrous methanol is poured in. The flask is closed off loosely with a cork. It is agitated intensively at 25°C for 1.5 hours, then the heating is switched on. After the suspension temperature reaches 50°C, it is agitated at this temperature for another half hour.

The yellow preparation mixture obtained is cooled in water with ice. The lemon-yellow hydride preparation is filtered off on a Schott G3 glass filter under reduced pressure, washing the sediment immediately with 10 mL of methanol twice and 10 mL of *n*-hexane twice. It is dried in a dessicator over solid KOH. 1.68 g of (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) hydride is obtained (88% yield).

(b) 0.692 g of (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) hydride is poured into a 100-mL measuring flask and 50 mL of benzene, 0.528 g of cyclopentadiene, and 0.2 g of sodium hydride are added. After mixing and closing the flask, it is allowed to stand for 5 days at 25°C. The subsequent procedure is as in Example 1, during which the filter with sediment is washed with benzene until the volume of colorless eluent reaches 300 mL. After evaporating the benzene off (preferably under reduced pressure), 0.115 g of ruthenocene is obtained (50% yield).

CLAIM(S)

1. Method for producing ruthenocene, characterized in that (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) hydride or halide with the general formula shown in the figure, in which X designates hydrogen or a halogen and L denotes triphenylphosphine, is heated in a medium of aromatic and/or aliphatic hydrocarbons at the boiling point of the solvent.

2. Method according to Claim 1, characterized in that an alkali metal or hydride of an alkali metal and cyclopentadiene are added to the reaction mixture, preferably in a molar excess several times that of ruthenium.

3. Method according to Claim 1, characterized in that a chloride is used as the halide of the original ruthenium compound.

4. Method according to Claim 1, characterized in that benzene, toluene, or *n*-hexane is used as the solvent.

5. Method according to Claim 2, characterized in that sodium or potassium is used as the alkali metal.

6. Method according to Claim 2, characterized in that sodium hydride is used as the alkali metal hydride.

7. Method of producing ruthenocene, characterized in that (π-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) hydride or halide with the general formula sown in the figure, in which X designates hydrogen or a halogen and L designates triphenylphosphine, is heated in a medium of aromatic and/or aliphatic hydrocarbons, maintaining it for five days at 25°C.

8. Method according to Claim 7, characterized in that an alkali metal or alkali metal hydride and cyclopentadiene are added to the reaction mixture, preferably in an excess of several times in relation to ruthenium.

9. Method according to Claim 7, characterized in that chloride is used as the halide of the original ruthenium compound.

10. Method according to Claim 7, characterized in that benzene, toluene, and/or *n*-hexane are used as the solvent.

11. Method according to Claim 8, characterized in that sodium and/or potassium are used as the alkali metal.

12. Method according to Claim 8, characterized in that sodium hydride is used as the alkali metal hydride.